J. Am. Chem. Soc. 1983, 105, 4955–4957

Novel Products in the Carbonylation of the Triply Bonded Ditungsten Hexaisopropoxide Dipyridine Adduct. 1. Synthesis and Structure of $[(i\text{-PrO})_3W(\mu\text{-CO})(\mu\text{-O-}i\text{-Pr})W(O\text{-}i\text{-Pr})_2py]_2$

F. Albert Cotton* and Willi Schwotzer

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843. *Received February 11, 1983*

Abstract: Treatment of $W_2(O\text{-}i\text{-Pr})_6py_2$ with CO in a mixture of hexane and toluene affords two products. One is $[(i\text{-PrO})_3W(\mu\text{-CO})(\mu\text{-O-}i\text{-Pr})W(O\text{-}i\text{-Pr})_2py]_2$, **1**, a centrosymmetric tetranuclear molecule in which the μ-CO groups form bridges via O–W bonds between the halves of the molecule, thus becoming η^2-μ_3-CO groups of an unprecedented type. This results in a $\overline{W-C-O-W-C-O}$ ring with a chair conformation. The W atoms involved in the rings are six-coordinate while the others are five-coordinate. This compound crystallizes in space group $P2_1/n$ with two tetranuclear units in the unit cell, each situated on an inversion center. The unit cell dimensions are a = 14.482 (12) Å, b = 16.909 (11) Å, c = 14.072 (9) Å, β = 115.10 (5)°, and V = 3120 (3) Å^3. The structure was refined to reliability indices of R_1 = 0.053 and R_2 = 0.063.

Several years ago Chisholm et al.[1] reported the reactions shown in Scheme I and described the structure of the compound $Mo_2(O\text{-}t\text{-Bu})_6(CO)$, which afforded the first example of a CO group bridging an M═M (double) bond. The reaction of CO with $Mo_2(O\text{-}i\text{-Pr})_6$ was more complex and gave a product that was only partially characterized; presumably the smaller size of $CH(CH_3)_2$ compared to $C(CH_3)_3$ permitted this more complex behavior. The chemistry of the $M_2(OR)_6$ compounds, like that of metal alkoxide chemistry generally, has been strongly dependent, throughout, on the steric effect of the R groups. In the case of the tungsten compounds, even the isolation of $W_2(O\text{-}i\text{-Pr})_6$ was impossible; the more complex tetranuclear $W_4(O\text{-}i\text{-Pr})_{14}H_2$ was obtained instead.[2] However, when the reaction of $W_2(NMe_2)_6$ with 2-propanol is carried out in the presence of pyridine (py), the compound $W_2(O\text{-}i\text{-Pr})_6py_2$ can be obtained.[3] More recently it has been shown that by addition of CO to $Mo_2(O\text{-}i\text{-Pr})_6$ in the presence of pyridine $Mo_2py_2(O\text{-}i\text{-Pr})_4(\mu\text{-O-}i\text{-Pr})_2(\mu\text{-CO})$ can be obtained,[4,5] and by addition of CO to $W_2py_2(O\text{-}i\text{-Pr})_6$ in the presence of pyridine the analogous $W_2py_2(O\text{-}i\text{-Pr})_4(\mu\text{-O-}i\text{-Pr})_2(\mu\text{-CO})$ is also available.[4] Thus, a general similarity in the chemistry of the dimolybdenum and ditungsten OR compounds with R = $C(CH_3)_3$ and $CH(CH_3)_2$ exists, although the details differ. Moreover, in each case many questions remain unanswered and there are gaps in our knowledge of their behavior.

We report here some observations that extend our knowledge and also throw some light on the course of previously observed reactions. Whereas Chisholm and co-workers have shown that the reaction of CO with $W_2(O\text{-}i\text{-Pr})_6py_2$ in the presence of additional pyridine follows the simple course represented by eq 1

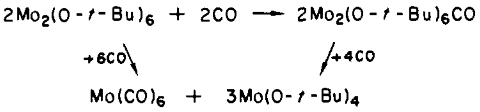
$$W_2(O\text{-}i\text{-Pr})_6py_2 + CO \rightarrow W_2(O\text{-}i\text{-Pr})_4py_2(\mu\text{-O-}i\text{-Pr})_2(\mu\text{-CO}) \quad (1)$$

we have found that when CO is added to a solution of $W_2(O\text{-}i\text{-Pr})_6py_2$ in toluene in which no additional pyridine is present, two different products are obtained, as shown in Scheme II. In this paper we report the synthesis and structural characterization of **1**. Product **2** will be described elsewhere.[6]

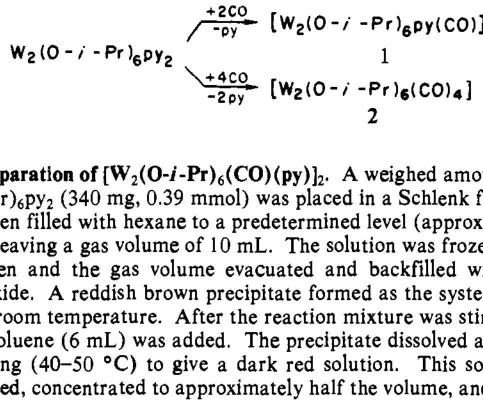
Experimental Section

General procedures, including the preparation of $W_2(O\text{-}i\text{-Pr})_6(py)_2$, have been described.[3]

Scheme I



Scheme II



Preparation of $[W_2(O\text{-}i\text{-Pr})_6(CO)(py)]_2$. A weighed amount of $W_2(O\text{-}i\text{-Pr})_6py_2$ (340 mg, 0.39 mmol) was placed in a Schlenk flask which was then filled with hexane to a predetermined level (approximately 10 mL), leaving a gas volume of 10 mL. The solution was frozen in liquid nitrogen and the gas volume evacuated and backfilled with carbon monoxide. A reddish brown precipitate formed as the system warmed up to room temperature. After the reaction mixture was stirred for 10 min, toluene (6 mL) was added. The precipitate dissolved after gentle warming (40–50 °C) to give a dark red solution. This solution was degassed, concentrated to approximately half the volume, and placed in a freezer at −20 °C. The title compound crystallized within 24 h. The mother liquor was once more concentrated to half its volume, and a second crop of crystals was obtained. The total isolated yield was 74% (240 mg).

X-ray Crystallography. A red plate of dimensions 0.6 × 0.6 × 0.15 mm was wedged into a glass capillary which was afterwards sealed at both ends. Unit cell dimensions were determined from 15 centered reflections with $2\theta \geq 24°$. Parameters pertaining to data collection and refinement of the structure are given in Table I. A preliminary data collection ($15° \leq 2\theta \leq 30°$) revealed an intensity distribution similar to that of a body centered cell. Significant violations were encountered, however, and the data were therefore collected for the primitive cell. Inspection of the complete data set ($4° \leq 2\theta \leq 50°$), including peak profiles, justified our choice, and no problems were encountered during solution or refinement of the structure in the $P2_1/n$ space group.

NMR Measurements. Proton-decoupled ^{13}C NMR spectra of the compound enriched with ^{13}CO (20% isotopic enrichment) were measured on a Varian XL-200 PFT spectrometer at 50.3 MHz. Spectra were also measured at 25.2 MHz on a JEOL PFT spectrometer in order to compare the dynamic behavior with that of Chisholm's $W_2(O\text{-}i\text{-Pr})_6(\mu\text{-CO})py_2$.[4]

Results and Discussion

The solid state structure of $[W_2(O\text{-}i\text{-Pr})_6py(CO)]_2$ consists of an ordered array of discrete molecules. The tetranuclear complexes are composed of identical W_2 subunits linked via the carbonyl ligands. An ORTEP drawing of the core is shown in Figure 1; a schematic diagram with the atom numbering scheme is shown

---

[1] (a) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7645.

[2] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Leonelli, J.; Little, D. *J. Am. Chem. Soc.* **1981**, *103*, 779.

[3] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.

[4] Chisholm, M. H.; Huffman, J. C.; Leonelli, J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 7030.

[5] Cotton, F. A.; Schwotzer, W. *Inorg. Chem.* **1983**, *22*, 387.

[6] Cotton, F. A.; Schwotzer, W. *J. Am. Chem. Soc.*, in press.

0002-7863/83/1505-4955$01.50/0

Table I. Crystallographic Data Collection Parameters

formula	$[W_2O_7NC_{24}H_{47}]_2$
fw	1658.6
space group	$P2_1/n$
a, Å	14.482 (12)
b, Å	16.909 (11)
c, Å	14.072 (9)
β, deg	115.10 (5)
V, Å^3	3120 (3)
Z	2
d_{calcd}, g/cm^3	1.765
cryst size, mm	plate 0.6 × 0.6 × 0.15
μ(Mo Kα), cm^{-1}	75.63
data collection instrument	Syntex P$\bar{1}$
radiation	Mo Kα
scan method	ω-2θ
data collection range, deg	4-50° (2θ)
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	2082
no. of parameters refined	297
R[a]	0.053
R_w[b]	0.063
quality-of-fit indicator[c]	1.19
largest shift/esd, final cycle	1.46
decay during data collection	41.4% (isotropic); corrected
absorption correction	semiempirical (ψ scan)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

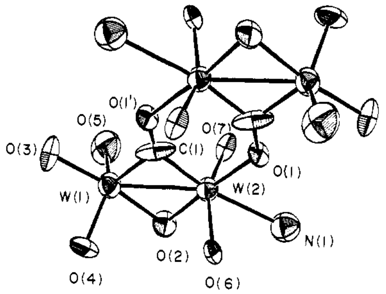


Figure 1. ORTEP view of the coordination sphere of $[(i\text{-PrO})_3W(\mu\text{-CO})(\mu\text{-O-}i\text{-Pr})W(\text{O-}i\text{-Pr})_2\text{py}]_2$.

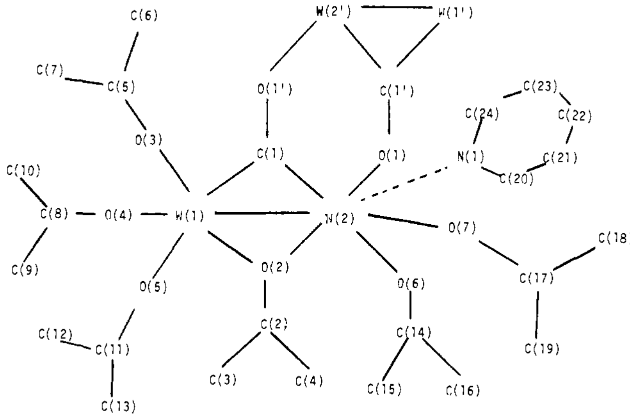


Figure 2. Connectivity and atom numbering scheme of $[W_2(\text{O-}i\text{-Pr})_6(\text{CO})(\text{py})]_2$.

Table II. Table of Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
W(1)	0.80414 (7)	0.49526 (6)	0.07227 (6)	3.55 (2)
W(2)	0.00619 (7)	0.49066 (5)	0.15131 (6)	3.07 (2)
O(1)	0.3920 (9)	−0.0077 (9)	0.4111 (9)	3.2 (3)
O(2)	0.086 (1)	0.5124 (9)	0.7742 (9)	4.1 (4)
O(3)	0.187 (1)	−0.004 (1)	0.440 (1)	4.2 (4)
O(4)	0.276 (1)	0.9012 (9)	0.608 (1)	5.5 (5)
O(5)	0.268 (2)	0.113 (1)	0.583 (1)	6.3 (7)
O(6)	0.462 (1)	0.0981 (8)	0.303 (1)	3.5 (4)
O(7)	0.473 (1)	0.8796 (8)	0.327 (1)	3.8 (5)
*N(1)	0.168 (2)	0.482 (1)	0.319 (2)	4.3 (5)
C(1)	0.405 (2)	0.001 (1)	0.510 (2)	5.2 (7)
C(2)	0.926 (2)	0.479 (2)	0.330 (2)	7.2 (9)
*C(3)	0.835 (4)	0.510 (3)	0.339 (4)	13 (2)
C(4)	0.049 (3)	0.597 (2)	0.627 (2)	8 (1)
C(5)	0.162 (2)	0.987 (2)	0.331 (2)	4.6 (6)
C(6)	0.158 (3)	0.071 (2)	0.287 (3)	9 (1)
C(7)	0.446 (3)	0.452 (2)	0.220 (2)	7 (1)
C(8)	0.176 (2)	0.856 (1)	0.564 (2)	4.9 (7)
C(9)	0.149 (3)	0.846 (3)	0.650 (3)	11 (1)
C(10)	0.204 (4)	0.773 (2)	0.539 (4)	17 (2)
C(11)	0.171 (3)	0.150 (2)	0.528 (2)	8 (1)
C(12)	0.190 (3)	0.233 (2)	0.504 (4)	11 (2)
C(13)	0.124 (4)	0.142 (3)	0.614 (4)	13 (2)
C(14)	0.510 (2)	0.822 (1)	0.676 (2)	4.4 (7)
C(15)	0.978 (3)	0.706 (2)	0.257 (3)	8 (1)
C(16)	1.091 (3)	0.725 (2)	0.171 (3)	8 (1)
C(17)	0.998 (3)	0.308 (1)	0.119 (2)	4.6 (8)
C(18)	0.962 (3)	0.251 (1)	0.183 (3)	8 (1)
C(19)	1.089 (2)	0.272 (2)	0.107 (2)	6.8 (9)
C(20)	1.204 (3)	0.543 (2)	0.380 (2)	5.9 (9)
C(21)	1.295 (3)	0.540 (2)	0.474 (2)	8 (1)
C(22)	0.351 (3)	0.469 (2)	0.498 (3)	8 (1)
C(23)	1.311 (3)	0.406 (2)	0.432 (3)	9 (1)
C(24)	1.218 (3)	0.415 (2)	0.344 (2)	7 (1)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Relevant Bond Lengths and Angles

	Bond Lengths, Å		
W(1)-W(2)	2.654 (1)	W(2)-O(1)	2.012 (14)
		-O(2)	2.012 (15)
-O(2)	2.075 (14)	-O(6)	1.917 (14)
-O(3)	1.921 (12)	-O(7)	1.905 (14)
-O(4)	1.910 (14)	-N(1)	2.52 (2)
-O(5)	1.92 (2)	-C(1)	1.91 (3)
-C(1)	2.00 (3)	O(1)-C(1')	1.33 (3)
	Bond Angles, deg		
W(2)-W(1)-O(2)	48.5 (4)	W(1)-W(2)-O(1)	134.3 (4)
-O(3)	140.4 (5)	-O(2)	50.6 (4)
-O(4)	103.7 (7)	-O(6)	100.4 (6)
-O(5)	103.2 (8)	-O(7)	99.5 (7)
-C(1)	45.9 (7)	-N(1)	144.4 (6)
O(2)-W(1)-O(3)	171.0 (6)	-C(1)	49 (1)
-O(4)	86.6 (8)	O(1)-W(2)-O(2)	175.1 (5)
-O(5)	88.5 (8)	-O(6)	90.9 (8)
-C(1)	94.4 (8)	-O(7)	89.4 (9)
O(3)-W(1)-O(4)	89.0 (8)	-N(1)	81.3 (7)
-O(5)	89.6 (8)	-C(1)	86 (1)
-C(1)	94.5 (9)	O(2)-W(2)-O(6)	88.2 (8)
O(4)-W(1)-O(5)	139 (1)	-O(7)	89.1 (9)
-C(1)	111 (1)	-N(1)	93.8 (7)
O(5)-W(1)-C(1)	110 (1)	-C(1)	99 (1)
O(7)-W(2)-N(1)	76.8 (7)	O(6)-W(2)-O(7)	151.8 (7)
-C(1)	104.0 (9)	-N(1)	75.4 (7)
N(1)-W(2)-C(1)	167 (1)	-C(1)	104.2 (9)
W(1)-C(1)-W(2)	85 (1)	W(2)-O(1)-C(1')	131 (2)
W(1)-C(1)-O(1')	131 (2)		
W(2)-C(1)-O(11)	143 (2)		

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits.

in Figure 2. Atomic coordinates with equivalent isotropic temperature factors are listed in Table II, and important bond angles and distances are given in Table III.

The tetranuclear complex is located on a crystallographic inversion center; each of the W_2 subunits possesses a local virtual mirror plane. The W–W bond is bridged by both an alkoxide group and a CO ligand. The two W atoms and the bridging C and O atoms form an approximately square-planar arranagement.

The coordination polyhedra around the tungsten atoms are different. The coordination number of W(1) is only five. The disposition of the five ligands, viz., three terminal alkoxide groups, Scheme III

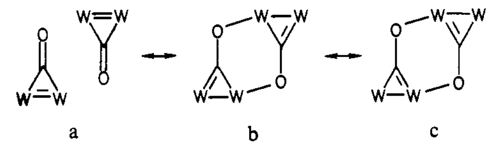


Table IV. NMR Data[a]

*C*O	310.4 ($^1J(\text{WC})_{\text{av}}$ = 172 (5) Hz)
py	150.4, 136.7, 123.5
$(\text{H}_3\text{C})_2\textit{C}\text{H}$	81.2, 77.1, 76.3, 76.1
$(\text{H}_3\textit{C})_2\text{CH}$	27.7, 27.3, 26.9, 25.0, 24.6

[a] ^{13}C chemical shifts in ppm relative to Me_4Si.

one bridging alkoxide group, and the bridging carbonyl group can be viewed as a distorted trigonal bipyramid. The axis is defined, approximately, by O(2)–W(1)–O(3), with an angle of 171.0 (6)°, due to bends of ca. 4.5° away from the equatorial ligand atom C(1). The other four axial-to-equatorial ligand angles, e.g., O(2)–O(4), O(2)–O(5) etc., are all in the range of 87–90°. The remaining three angles, which would ideally be 120° are in fact 110°, 111°, and 139°, indicating that O(4) and O(5) are each ca. 10° off of their ideal positions. The coordination geometry around W(2) can be described as distorted octahedral. The trigonal bipyramid and the octahedron are sharing the C(1)–O(2) edge which is intersected by the W–W bond vector. The W–W bond is significantly longer at 2.654 (1) Å than the M–M bonds in $\text{Mo}_2(\text{O-}i\text{-Pr})_6\text{py}_2(\text{CO})$ or $\text{W}_2(\text{O-}i\text{-Pr})_6\text{py}_2(\text{CO})$ (2.486 (2) and 2.499 (3) Å, respectively[4,5]) and falls within the range typical for W–W single rather than double bonds.[7]

The distribution of bond lengths and angles within and around the CO fragment is remarkable. We find the CO bond length increased to 1.33 (3) Å as compared to 1.198 (8)° in $\text{Mo}_2(\text{O-}i\text{-Pr})_6\text{py}_2(\text{CO})$. In addition, the O(1)–W(2)′ distance of 2.01 (1) Å indicates that there is a substantial bonding interaction between these two atoms. The electronic nature of this interaction can be described by the resonance hybridization depicted in Scheme III, with **c** predominating over **b** in view of the fact that the W(2)–C(1) distance, 1.92 (2) Å, is shorter than the W(1)–C(1) distance, 1.99 (3) Å.

The type of η^2-μ_3-CO group found in this compound is without precedent, so far as we know. The nearest thing to it would be the Lewis acid adducts in which an aluminum halide[8] or an ytterbium–bis(pentamethylcyclopentadienyl) complex[9] is attached to the oxygen atom of a bridging carbonyl group.

NMR Spectra. In view of the unprecedented structure found in the crystalline compound information about the structure in solution was sought from NMR spectra. Proton-decoupled ^{13}C spectra at ambient temperature were recorded on benzene solutions at two spectrometer frequencies (50.4 and 25.2 MHz). The results are summarized in Table IV. The spectra at the two frequencies are essentially equivalent and display a pattern of resonances for the isopropyl carbon atoms that is consistent with the solid-state structure. Five separate methyl resonances are resolved but, presumably, two of the expected five α-carbon resonances are accidently superposed. These observations show that alkoxide scrambling does not occur on the NMR time scale, in contrast to Chisholm's observation[4] that under comparable conditions $\text{W}_2(\text{O-}i\text{-Pr})_6\text{py}_2(\text{CO})$ does show exchange of the isopropoxy groups.

Turning now to the ^{13}CO resonance, we find almost the same chemical shift as that found[4] in $\text{W}_2(\text{O-}i\text{-Pr})_6\text{py}_2(\text{CO})$. This is surprising since this resonance might be expected to show considerable sensitivity toward changes in composition and structure. For example, it is known[4] that for $\text{W}_2(\text{OR})_6\text{py}_2(\text{CO})$ a change in R from *i*-Pr to *t*-Bu causes a downfield shift of 9.2 ppm. Dimerization as observed in the crystal would be expected to shift the resonance. It seems likely, therefore, that the predominant species in solution is, in both cases, the tetranuclear species and that the following equilibrium prevails

$$2\text{W}_2(\text{O-}i\text{-Pr})_6\text{py}_2(\text{CO}) = [\text{W}_2(\text{O-}i\text{-Pr})_6\text{py}(\text{CO})]_2 + 2\text{py}$$

Presumably when the solution is prepared from $\text{W}_2(\text{O-}i\text{-Pr})_6\text{py}_2(\text{CO})$, the equilibrium lies well to the right, but rapid, dynamic equilibrium allows O-*i*-Pr scrambling to occur via the fluxional $\text{W}_2(\text{O-}i\text{-Pr})_6\text{py}_2(\text{CO})$ species, or possibly some other fluxional species. When a solution is prepared from $[\text{W}_2(\text{O-}i\text{-Pr})_6\text{py}(\text{CO})]_2$, this tetranuclear species is long-lived on the NMR timescale.[10]

Unfortunately little information is available from ^{183}W satellites because of a superposition of lines from different isotopomers. For any given fragment, $^{183}\text{W}{-}^{x}\text{W}{-}^{13}\text{C}$, there are three almost equally probable combinations with X = 182 (26.4%), 184 (30.6%), and 186 (28.4%) obscuring possible differences between the $^1J(^{183}\text{W}(1){-}\text{C}(1))$ and $^1J(^{183}\text{W}(2){-}\text{C}(1))$ coupling constants. The central line (arising from isotopomers with W(1) and W(2) $\neq$ ^{183}W) is broadened for the same reason, and possible satellites due to ^2J couplings (across the carbonyl oxygen atom) could not be assigned with certainty.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

Registry No. 1, 85956-37-2; $\text{W}_2(\text{OPr-}i)_6\text{Py}_2$, 70178-75-5; W, 7440-33-7.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic thermal parameters (13 pages). Ordering information is given on any current masthead page.

---

(7) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(8) Kim, N. E.; Nelson, N. J.; Shriver, D. F. *Inorg. Chim. Acta* **1973**, *7*, 393.

(9) Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.*, **1981**, 985.

(10) An attempt to corroborate this proposal by infrared spectroscopy was inconclusive, as will now be explained. Following the procedure of ref 4, CO was added to $\text{W}_2(\text{O-}i\text{-Pr})_6\text{py}_2$ in the presence of excess pyridine. When the reaction mixture is cooled, only a brown amorphous (or perhaps very finely crystalline) precipitate was obtained. This procedure was repeated several times, always with the same result. Since it had been our intention first to identify the $\text{W}_2(\text{O-}i\text{-Pr})_6(\text{CO})\text{py}_2$ compound by its unit cell dimensions and then compare its IR spectrum with that of **1**, failure to obtain crystals was critical. The reaction mixture was warmed to room temperature (which caused a considerable amount of the brown precipitate to go into solution) and set aside at −20 °C. The only crystals to grow were the characteristic red cubes of **1**. The IR spectrum of these crystals does not, of course, show the bands at 1601 and 1555 cm^{-1} reported for $\text{W}_2(\text{O-}i\text{-Pr})_6(\text{CO})\text{py}_2$. In summary, we have been unable to obtain a crystalline sample of the latter compounds.